Application of Thermal Cracking Mechanism of Chrysene Molecule Using Density Functional Theory

M.A. Shanshal[1] and Q.A.Yousif[2*]

1. Department of Chemistry, College of Science, Baghdad University, Baghdad, Iraq

2. Department of Chemistry, College of Science, Al-Qadissya University, Al-Qadissya, Iraq

Abstract: Density functional theory calculations were carried out to study the thermal cracking for chrysene molecule to estimate the bond energies for breaking C10b-C11, C11-H11 and C4a-C12a bonds as well as the activation energies. It was found that for C10b-C11, C11-H11 and C4a-C12a reactions, it is often possible to identify one pathway for bond breakage through the singlet or triplet states. Thus, the C11-H11 and C11-C10b bonds ruptured in triplet state whilst the C12a-C4a in singlet state. Also, it was fond that the activation energy value for C4a-C12a bond breakage is lower than required for C10b-C11 and C11-H11 bonds that enquired the C4a-C12a bond "bridge bond" is a weaker and ruptured firstly in thermal cracking process. It seems that the characteristic planarity for polyaromatic hydrocarbons is an important factor to acquire the molecule structure the required stability along the reaction paths as well as the full octet rule and Clar's π-sextet structure, especially when chrysene molecular lose the property of planarity. The atomic charges supported the observation that the breaking bonds C10b-C11, C11-H11 and C4a-C12a in triplet or singlet states. The configurations in transition state and the conformation for the end products reaction were explained and discussed.

Key words: DFT, chrysene, thermal cracking, C-C rupture, C-H rupture.

1. Introduction

The crude oil or oil residue can be classified according to its saturate, aromatic, resin and asphaltene components [1]. Poly aromatic hydrocarbons are present in high concentrations in crude oil [2]. Thermal cracking or pyrolysis is considered as the dominant reaction mechanism during Kerogen maturation and oil and gas generation in the geological environment [3]. The C-H and C-C bonds rupture reactions are basic for the thermal of aromatic hydrocarbons [4]. The bond dissociation energy "BDE" is essential a probe for the reaction enthalpy of the homolytic cleavage of the considered bond. The BDE is a good indicator of chemical reactivity since it represents a reliable measure of bond strength [5]. The bulk of the experimental of the physical properties to polyaromatic aromatic hydrocarbon "PAHs" have been to identify the vibrational frequencies [6]. It is much more difficult to determine experimentally the C-H and C-C BDEs of these large species compared to monocyclic compounds and thus experimental C-H and C-C BDEs of the "PAHs" are very scarce in the literature. Therefore, a lot of researchers have focused on the accurate theoretical calculation of BDEs [4-6]. The aim of this work is to use computational methods to study the C12a-C4a, C11-C10b and C11-H11 BDEs of chrysene molecule one of the polyaromatic hydrocarbons via the hybrid DFT B3LYP method.

2. Computational Method

All DFT calculations were performed using the Gaussian09 program [7] running on the workstation that have the high performance in a CPU and memory size. The B3LYP function in conjugation with the 6-311G [8, 9] basis set was used to optimization

Corresponding authors: Qhatan A. Yousif, Processor, research fields: quantum and physical chemistry. E-mail: qhatanas101@yahoo.com.

geometries. This level of theory is known to provide a quantitatively good description of geometries which has, in particular, been shown for radical study at the PAHs [5]. All DFT involving computations the open-shell radical species were performed using the unrestricted methodology [9].

3. Results and Discussion

The energies required to break C12a-C4a, C11-C10b, C2-H2 and C1-H1 bonds have been calculated by virtue of the singlet and triplet state. By examining the potential energy curves one can deduce whether a particular reaction pathway for bond breakage is favoured in comparison with other pathways. However, for the C11-C10b, C2-H2 and C1-H1 bonds reactions, it is possible to identify one pathway for bond breakage through the triplet state and C12a-C4a bond reaction at singlet by employing the density functional theory. The carbon and hydrogen atoms of the chrysene molecule are numbered in conformity with the convention laid down by the International Union of Pure and Applied Chemistry "IUPAC" for regular naming of chemical compounds. The values for the activation energy (136.968 kcal/mol) at bond length 2.8Å and the reaction energy (114.5480 kcal/mol) at the bond length 2.9Å via a singlet state pathway are exhibited in Fig. 1.

Scheme. 1 can be invoked to discuss the reaction mechanism that includes the cleavage of the C12a-C4a
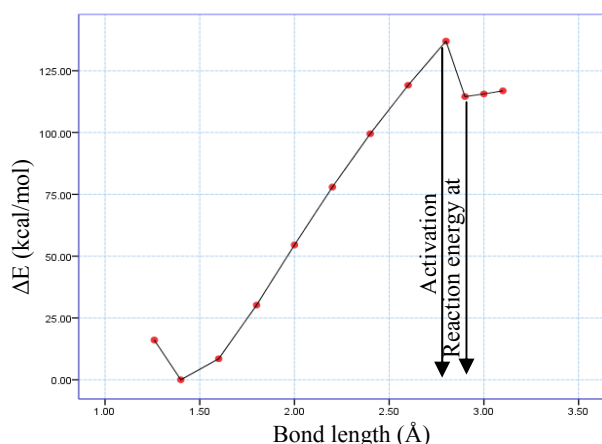
bond via a transition state structure, including the atomic charges for all atoms in the molecule. Firstly in the transition state, the closed chain of the hydrocarbon is configured that contains resonance and double bonds. The allene fragment (the atom C12a is central to the allene) is constituted and shared by the resonance process with other carbon atoms. So, all the atoms conform to a stable octet number rule [10, 11] without loss of planarity. In the singlet state (bond length 2.9 Å) the closed distorted chain of the hydrocarbon is formed that contains single and double bonds. The allene fragments is constituted and unshared with carbon atoms through the resonance process. Thus, all the atoms reach a stable electronic octet [10, 11].

Likewise, Fig. 2 shows the atomic charges for C12a and C4a which confirms that the C12a-C4a breaks beyond a bond length of 2.8Å.

The activation energy value (158.4086 kcal/mol) at the bond length 3.4Å and the reaction energy value (131.1401 kcal/mol) at the bond length 3.5Å following the singlet state pathway are shown in Fig. 3.

The mechanism of the reaction that includes a transition state structure and the breaking of the C10b-C11 bond are described by means of Scheme 2.

In the transition state, the benzene ring is opened between the carbon atoms (C10b and C11). The occurrence of rotation around the C4a-C4b bond axis with loss of planarity as a result leads to the strong interactions between the following atoms (the carbon atom C10b with C6, the hydrogen atoms H1 with H12; H4 with H5 and H11 with H10). In the triplet state, the occurrence of greater rotation around the C4a-C4b

Fig. 1   Potential energy curve for chrysene molecule for C12a-C4a bond breakage.
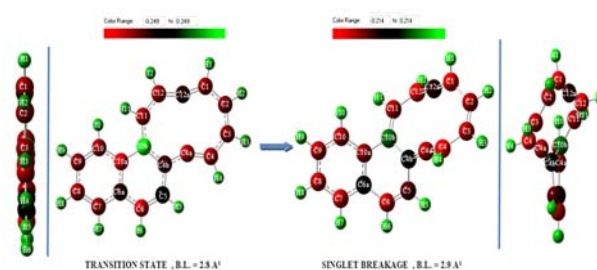
Scheme. 1   Transition state, the product of the cleavage of the C12a-C4a bond, and the atomic charges for each the atoms (distinguished by means of colour).
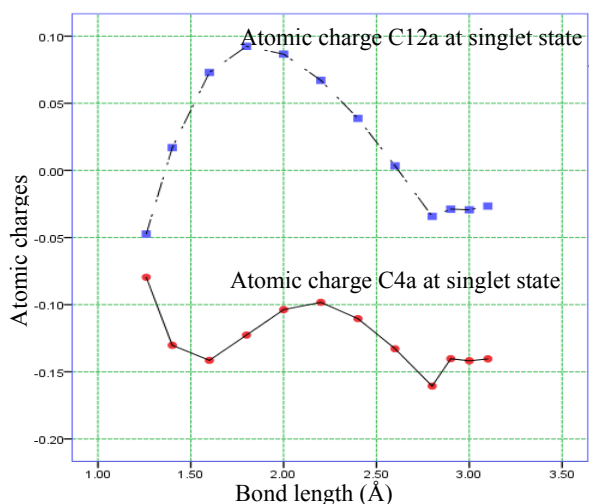
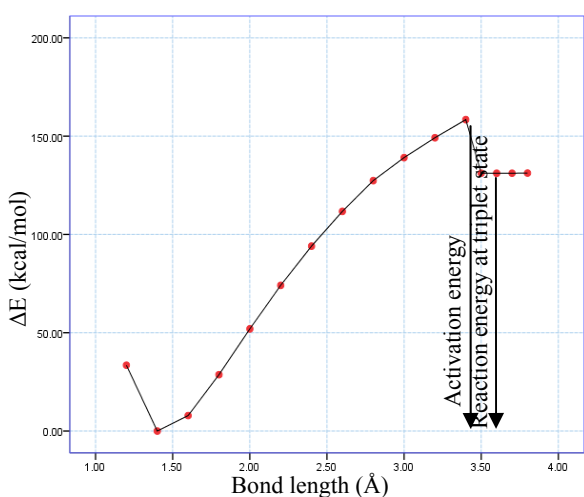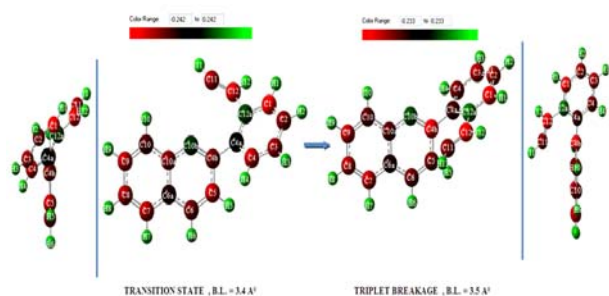**Fig. 2   Atomic charges for C12a and C4a for chrysene molecule.**

Fig. 3   Potential energy curve for chrysene molecule for C11-C10b bond breakage.

Scheme. 2   Transition state, the product of the cleavage of the C10b-C11 bond, and the atomic charges for each the atoms (distinguished by means of colour).

bond axis with loss of planarity, leading to a reduction in the aforementioned strong interaction. Consequently, this modification gives the required stability for the

molecule structure owing to a reduction in the overlap of the orbitals between the ethylene and naphthalene fragments. At the same time, this enhances the overlap of the orbitals for the naphthalene part and accomplishes a greater distribution of electron density on both sides of the molecule (see the electrostatic potential map "ESP").

Thus, Fig. 5 confirms the cleavage of the C10b-C11 bond at a bond length of 3.5 Å.

The activation energy value (154.9645 kcal/mol) at the bond length 4Å and the reaction energy value (115.1715 kcal/mol) at the bond length 4.1Å following the triplet state pathway are shown in Fig. 6. The mechanism of the reaction that includes a transition state structure and the breaking of the C11-H11 bond is described by means of Scheme. 3.
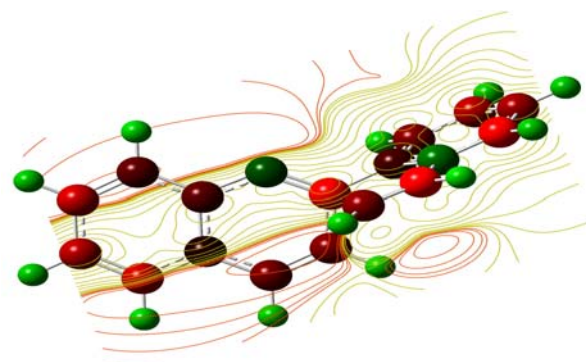

Fig. 4   ESP for chrysene molecule for C11-C10b bond breakage.
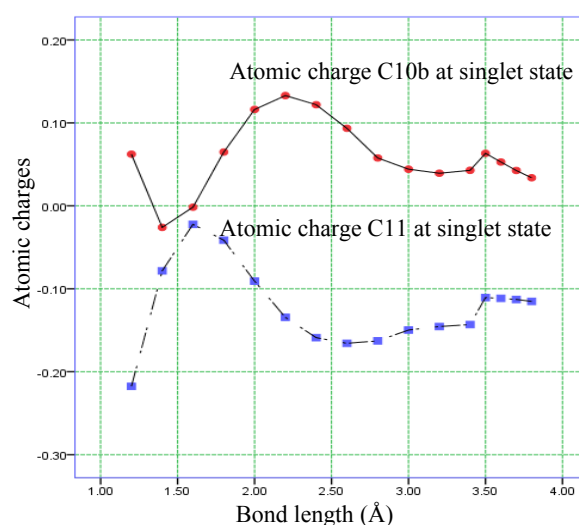

Fig. 5   Atomic charges for C10b and C11 for chrysene molecule.

In both states, the hydrogen atom (H11) is moved away from the molecule with retention by the same plane in the sense that the interaction is experienced equally by the hydrogen atoms (H11) and (H10, H12). Thus, at a bond length of 4.1Å in triplet state the hydrogen atom H11 is moved away from the molecule as a free radical and moved far from the planar molecule. Thus, the two (Clar's π-sextet structure) have been configured and both structures preserve the planarity characteristic of aromatic compounds. The conversion of atomic charges for carbon atom C11 and hydrogen atom H11 from positive values into negative values and to a value that is close to zero that suggests that the release of the hydrogen atom H11 as a free radical occurs without any interactions with other atoms (this is shown in Fig. 7. Moreover, Fig. 7 provides evidence for the cleavage of the C11-H11 bond at the aforementioned length.
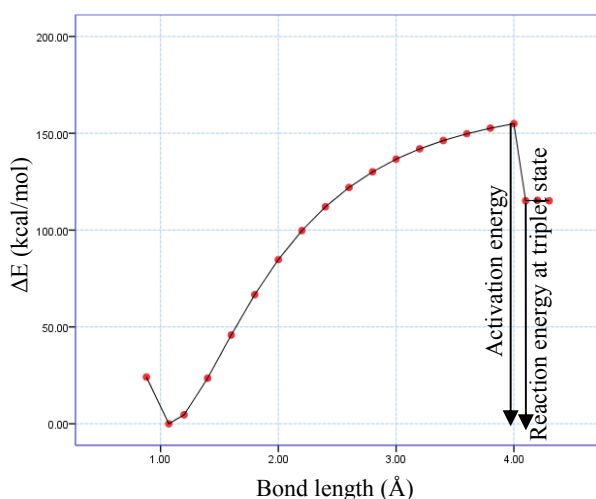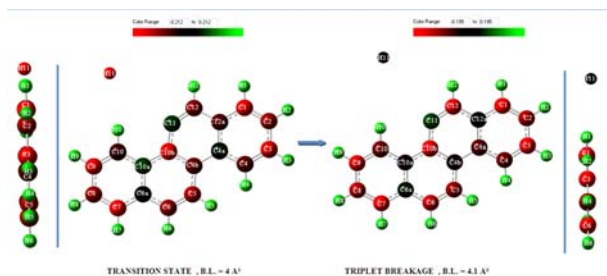

Fig. 6   Potential energy curve for chrysene molecule for C11-H11 bond breakage.

Scheme. 3   Transition state, the product of the cleavage of the C11-H11 bond, and the atomic charges for each the atoms (distinguished by means of colour).
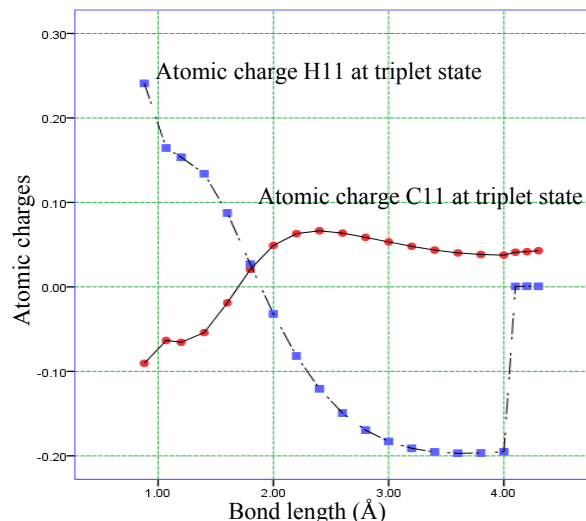

Fig. 7   Atomic charges for C10b and C11 for chrysene molecule.

4. Conclusions

The activation energies values is arranged in the following sequence C10b-C11 > C11-H11 > C4a-C12a. The low activation energy value for C4a-C12a bond due to the transition state is full octet. Thus, the low activation energy value C11-H11 bond owing to the transition state is completely planar and have the good variation atomic charges via a bond length and the C11 carbon atom is retained of a positive charge values as a proceed reaction. There are different mechanisms to describe the cleavage C12a-C4a, C11-C4a bond as results to different end products. As C4a-C12a bond in chrysene molecule is weaker than C11-H11 and C10b-C11 bonds, it is reasonable to presume that C4a-C12a bond is broken first when chrysene molecule is exposed to thermal cracking.

References

[1]   Castellano, O.; Gilman, R. Therotical Study of Interaction in Hetroatomic Moncyclic Molecular Complexes of Benzene, Pyridine and Thiophene Dimmers. *Energy Fuels* **2011,** *25,* 2526-2541.

[2]   Olah, G. A. *Hydrocarbon Chemistry;* John, Wiely & Sons: New York, 2003.

[3]   Meng, X.; Xu, C. Catalytic and Thermal Pyrolysis of Atmospheric Residue. *Energy & Fuels* **2003,** *23,* 65-69.

[4]   Shanshal, M.; Muala, M. M. Reaction Paths and Transition States of C-H Bond Rupture in Aromatics, Benzene and Toluene. *Jordan Journal of Chemistry* **2011,** *6,* 165-173.

[5]   Hemloset, K.; Van, V. Specybroeck Bond Dissociation Enthalpies of Large Aromatic Carbon-Carbon Radical. *J. Phys .Chem. A* **2008,** *122,* 13566-13573.

[6]   Barkholt, C.; Hadad, C. M. C-H and N-H Bond Dissociation Energy of Small Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1999,** *121,* 491-504.

[7]   Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G.

E.; Robb, M. A.; Cheeseman, J. R.; et al. I*nformation & Communications;* the National Academy of Science: USA, 2009.

[8]   Sholl, D. S.; Steckel, J. A. *Density Functional Theory;* John Wiely: New York, 2009.

[9]   Bachrach, S. M. *Computational Organic Chemistry;* John Wiely: New York, 2007.

[10] Smith, M. B.; March, J. *March's Advanced Organic Chemistry;* Jonh Wiely: New York, 2007.

[11] Smith, J. G. *Organic Chemistry;* McGraw & Hill Press: New York, 2011.